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Heteroepitaxy of large grain Ge film on cube-textured Ni(001) foils through CaF_2 buffer layer

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ABSTRACT

Cube-textured Ni(001) foils have been considered as a viable alternative substrate to grow high quality functional films for large area optoelectronic devices. In this work, we report the heteroepitaxial growth of $CaF_2(001)$ films on cube-textured Ni(001) foils at 350–600 °C with in-plane orientation of $CaF_2[110]$//Ni[100] and $CaF_2[\bar{1}10]$//Ni[010] with 45° rotation respect to the Ni(001) substrate. Unlike $CaF_2(111)$/Ni(001) films where there exist four independent rotational domains with rotational domain boundaries, $CaF_2(001)$/Ni(001) contains no rotational domains or rotational domain boundaries. This makes $CaF_2(001)$/Ni(001) films better candidates as templates for the growth of high quality functional semiconductors. We also demonstrate that Ge(001) film with no rotational domains and with a grain size of ~50 μm similar to that of the Ni substrate can be grown on the $CaF_2(001)$ buffered Ni substrate.

1. Introduction

Semiconductor films grown on amorphous surfaces *via* biaxially textured buffer layers have attracted considerable interest recently due to their potentially low cost and large scale fabrication capability [1–9]. Biaxial textured films, which have both strong preferred out-of-plane and in-plane orientations, have been grown by either oblique angle deposition [10–17] or ion beam assisted deposition [3,18–20] on amorphous or polycrystalline substrates, *e.g.*, glass and metal foils. Functional semiconductors such as Si [1,3,5,8,21], Ge [9,22,23], CdTe [4,7], GaAs [24] and GaN [2] films have been grown heteroepitaxially with small angle grain boundaries on biaxial buffer layers. The small angle grain boundaries are believed to be benign to the electrical properties of semiconductors [1,25].

The fabrication of Ni based biaxial metal sheets using the rolling-assisted-biaxially-textured-substrates (RABiTS) process opens up an important direction to study biaxial large-scale, flexible semiconductors or superconductor devices [6,23,26–29] on these low cost Ni sheets. CdTe(111) film has been successfully grown on a cube-textured Ni substrate heteroepitaxially [4,30] for photovoltaic applications. However, the CdTe(111) film has four independent rotational domains due to the four-fold symmetry of the Ni(001) substrate. Dutta et al. also demonstrated the growth of the heteroeptaxial Ge(001) film on Ni(001) using a CeO_2 buffer layer [23]. Ge film growth has also been tried on the cube-textured Ni substrates directly [31]. Results indicate that the heteroepitaxial growth of Ge(111)film on Ni(001) can be with the intermediate deposition of a CaF_2 (111) buffer layer deposited on the Ni substrate to prevent the severe alloying between Ge and Ni. Four rotational domains were still observed in the $CaF_2(111)$ buffer layer on Ni(001) as well as the Ge(111) film.

In this paper, we report the epitaxial growth of a $CaF_2(001)$ buffer layer on cube-textured Ni(001) foil for Ge(001) film growth that results in no rotational domain. The epitaxial growth conditions of the CaF_2 buffer layer on the Ni substrate, especially the CaF_2 growth temperature and the cleaning procedure of the Ni substrate, were studied. We found that after a pure hydrogen gas annealing of the Ni substrate, the CaF_2 grewwith [001] orientation and with no rotational domains. On the other hand, using a forming gas (3% hydrogen) annealing of the Ni substrate, the CaF_2 film grew with [111] orientation and four independent rotational domains. The different orientation growth selections are quite similar to the observed heteroepitaxial growth of CdTe films on GaAs(001) substrates [32–35], where the CdTe films can also have two different growth orientations, (111) and (001). We have also demonstrated that Ge(001) with no rotational domains can be grown on the $CaF_2(001)$/Ni(001) substrate at 400 °C. This Ge film also exhibits large grain size similar to that of the Ni substrate.

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2. Experimental

For all depositions, the 1 cm × 1 cm × 75 μm Ni foil substrates were cleaned in a sonication bath using trichloroethylene, acetone, methanol, and isopropyl alcohol sequentially, for 15 min each. Then the sample was blown dry using dry air before putting into the vacuum chamber. The cube-textured Ni(001) sheet had a biaxial texture with grain sizes of 50–150 μm. The evaporator was a home-made stainless vacuum chamber pumped by a turbo pump and backed up by a mechanical pump to a base pressure of 6.6×10^{-6} Pa. The chamber was equipped with a gas handling system for hydrogen or forming gas. The gas was continuously fed into the chamber during annealing. The Ni substrate was annealed either in a forming gas environment (97% N_2 + 3% H_2) or an ultra high purity (UHP) hydrogen environment. The pressure of each gas was kept at 13 mPa for the oxide reduction cleaning of Ni substrates. CaF_2 films and Ge films were grown by thermal evaporation using tungsten filament baskets and alumina coated tungsten filament baskets for housing CaF_2 and Ge crystals, respectively. The Ni substrate was mounted upside-down on a heating stage (button style resistive heating) using Mo clamps. The CaF_2 and Ge sources were mounted about 10 cm below the substrate. A thermocouple was mounted on the surface of the sample to record the temperature during all experiments. Before the depositions, the gases were pumped out until the base pressure reached ~1.3×10^{-5} Pa. The thicknesses of the CaF_2 film and Ge film were 750 nm and 300 nm, respectively according to an *ex situ* SEM (scanning electron microscopy) cross section image. The deposition durations were about 40 min for each film.

One CaF_2 film was grown at 350 °C on a Ni substrate, which was previously annealed at 350 °C *in-situ* for 1 h in the forming gas environment. We label this 'Sample A' in the following text. Another CaF_2 film was grown at 350 °C on a Ni substrate, which had previously been annealed at 400 °C *in-situ* for 5 h in the forming gas environment. We label this 'Sample B' in the following text. Another set of CaF_2 films was grown at four different Ni substrate temperatures of 350 °C, 425 °C, 500 °C, and 600 °C, labeled 'Sample C_1', 'Sample C_2', 'Sample C_3' and 'Sample C_4', respectively. The Ni substrate cleaning conditions were consistent for these samples; they were annealed at 400 °C *in-situ* for 3 h in a (UHP) hydrogen environment based on established procedures for surface oxide reduction on Ni surfaces [36–38]. A summary of the substrate cleaning conditions and the CaF_2 deposition conditions are listed in Table 1.

One Ge/CaF_2/Ni sample was also prepared. For this sample, the Ni substrate was annealed at 400 °C *in situ* for 3 h in a (UHP) hydrogen environment; the CaF_2 was then deposited at 350 °C and followed by the deposition of Ge at 400 °C without breaking vacuum. The texture orientations of each of these films were studied *ex situ* by x-ray diffraction (XRD) and x-ray pole figure technique using a PanAlytical X'Pert Pro X-ray Diffractometer. The surface morphologies of some of the samples were imaged using a ZEISS SUPRA 55 FE scanning electron microscope (SEM). A layer of Pt was deposited on the sample before the cross section of the sample was prepared by focus ion beam (FIB) milling. Electron back scattered diffraction (EBSD) was performed in a Carl Zees ultra 1540 dual beam FIB/SEM system with 15 keV electron beam energy.

3. Results and discussion

3.1. CaF_2 (111) vs. CaF_2 (001) films grown on Ni(001) substrates with different substrate cleaning procedures

We first studied the procedures for Ni surface cleaning by using different annealing and deposition temperatures, different annealing gases and different annealing durations. The last column in Table 1 is a summary of the dependence of texture orientation on these parameters. Fig. 1(a) shows the XRD theta-2theta scan of Sample A (black curve) where the Ni(001) substrate went through the forming gas 1 h annealing at 350 °C. The CaF_2 film deposition was performed at the substrate temperature 350 °C. Only the (111) peak corresponding to CaF_2 was observed. Fig. 1(b) is a top view SEM image of the CaF_2(111) surface of Sample A. There is only one type of morphology consisting of triangle-shaped features over the entire sample surface. The majority of these features are parallel to one another as shown in the inset of Fig. 1(b). Fig. 1(a) also shows the XRD theta-2theta scan of Sample C1, CaF_2(001) film on Ni(001) substrate (red curve). The Ni(001) substrate went through a pure H_2 gas annealing at 350 °C for 3 h before CaF_2 film deposition. The CaF_2 film deposition was performed at the substrate temperature, 350 °C. The dominant growth orientation of the CaF_2film is the [001] direction on the Ni(001) substrate. The double-peak of CaF_2(004) scan corresponds to the diffraction from Cu $k_{\alpha 1}$ and Cu $k_{\alpha 2}$ generated by the x-ray source. Note the ratio of the Cu $k_{\alpha 1}$/Cu $k_{\alpha 2}$ is ~2 in our measurement condition. This indicates better crystal quality in Sample C_1 as compared to Sample A. Fig. 1(c) is a top view SEM image of the CaF_2(001) surface of Sample C_1. Two different morphologies are observed and are randomly distributed over a large area of the sample surface. The insets of Fig. 1(c) are zoomed-in SEM images of two different types of morphologies observed. One type (left inset) has square shapes with ridged edges, and the other type (right inset) has larger irregular triangle shapes tilted more relative to the substrate plane. Both morphologies have been observed in CaF_2(001) films grown on Si(001) by others [39,40].

XRD theta-2theta scans reveal only the out-of-plane growth orientation. To gain more information about the texture orientation, the XRD pole figure technique was used to characterize the samples. Fig. 2(a) is the Ni{111} pole figure of a Ni substrate without a CaF_2 film deposited on it, to serve as a reference. We see four separated poles distributed symmetrically about the origin at chi angle χ ~ 54° as expected given the (001) oriented biaxial texture of Ni. Note that chi angle (polar angle from the normal direction of the substrate) is measured outward from the center of the pole. Fig. 2(b) is the CaF_2{111} pole figure of Sample A, the Ni substrate of which was treated by the forming gas for 1 h at 350 °C. The center pole indicates the [111] out-of-plane orientation, which has been confirmed by the XRD theta-2theta scans. However, there are 12 poles azimuthally distributed evenly at χ ~ 71°. Ideally for one orientational domain, there should exist only three poles located at χ ~ 71° in the {111} pole figure. In our CaF_2 film, there are actually four sets of three poles at χ ~ 71°, indicating four independent rotational domains. All four sets share the same center pole. Different sets of poles are labeled with different colored circles. Fig. 2(c) is the CaF_2{111} pole figure from Sample B, the substrate of which was annealed by the

Table 1
Ni(001) substrate surface cleaning and deposition conditions for the samples studied. The table also shows the out-of-plane crystal orientation of the CaF_2 films under different substrate cleaning and deposition conditions.

Ni annealing gas	Sample number	Ni annealing temperature (°C)	Ni annealing time (hours)	CaF_2 deposition temperature (°C)	CaF_2 epitaxial growth orientation
Forming gas with 3% H_2	A	350	1	350	CaF_2(111)
	B	400	5	350	CaF_2(111) and CaF_2(001)
Ultra high purity hydrogen gas	C_1	400	3	350	CaF_2(001)
	C_2	400	3	425	CaF_2(001)
	C_3	400	3	500	CaF_2(001)
	C_4	400	3	600	CaF_2(001)